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AN INVESTIGATION OF THE IGNITION DELAY TIMES FOR PROPYLENE OXID--ETC(U)
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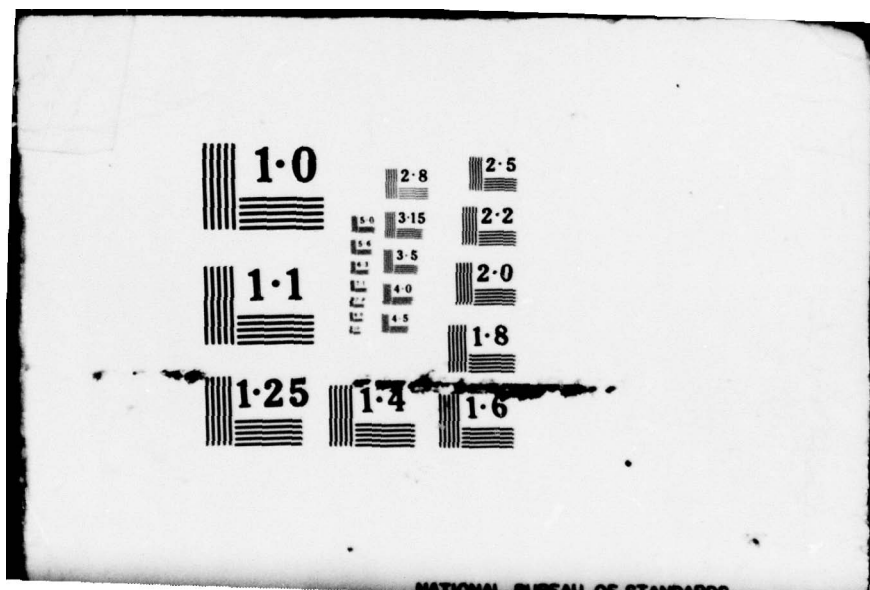
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AN INVESTIGATION OF THE IGNITION DELAY TIMES
FOR PROPYLENE OXIDE-OXYGEN-NITROGEN MIXTURES.

by

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Earl Edward Meister, III

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AN INVESTIGATION OF THE IGNITION DELAY TIMES
FOR PROPYLENE OXIDE-OXYGEN-NITROGEN MIXTURES

ABSTRACT

A reflected shock tube technique has been used to measure the ignition delay time for propylene oxide-oxygen-nitrogen mixtures in the temperature range of 900 to 1250°K. Mixture equivalence ratios ranging from $\phi = 0.8$ to $\phi = 1.25$ were used. Ignition delay times were measured by using both streak schlieren and pressure gauges mounted on the back wall of the shock tube. A regression analysis indicated that the delay time multiplied by the propylene oxide concentration to the .8 power and the oxygen concentration to the -1.2 power yielded a best fit when plotted as a logarithm against the reciprocal temperature. This regression analysis also indicated that the nitrogen concentration had no effect on the ignition delay time. The apparent activation energy for the reaction was found to be approximately 19 kcal or 1.6×10^6 joule/mole.

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I. INTRODUCTION

In the past few years an increasing number of experimental studies have been conducted on modeling the ignition delay times involved in fuel-air explosions. Reasons for these studies can be attributed to the search for alternative fuel sources, to the prevention of explosions occurring after accidents involving highly combustible fuels, and to the development of fuel-air explosion weaponry.

A literature search revealed that recent research in fuel-air explosions has been conducted using propylene oxide [1,2]. Yet there appears to be a lack in the literature of any ignition delay models involving propylene oxide which might aid in analyzing these results. An ignition study was conducted by Hikita and Yoneda using a shock tube [3]. An abstract of their report [4] shows that in propylene oxide-oxygen-argon mixtures with fuel equivalence ratios between 0.333 and 2.67, the rate controlling reaction's activation energy is 1.76×10^5 joule/mole (42.1 Kcal/mole). No mention was made of the concentration dependency of the overall rate.

In this investigation the activation energy and the concentration dependencies of the rate controlling reaction in the ignition of propylene oxide-oxygen-nitrogen mixtures are determined by correlating the experimental data to the Arrhenius relation: $t_i = A \exp(E/RT) [C_3H_6O]^a [O_2]^b [N_2]^c$.

II. EQUIPMENT

A. University of Illinois Shock Tube

The ignition study, described in this investigation, was conducted using the buffer chamber and the low pressure chamber of the Aeronautical and Astronautical Engineering Department's rectangular shock tube. A brief description of the shock tube follows; a more detailed description can be found in Reference 5.

The buffer chamber, used as the high pressure (compression) chamber, is 4.04 meters long and has an internal cross section of 0.1016 x 0.381 meters.

The low pressure chamber is separated into two sections: an expansion section 8.64 meters long and a test section 0.864 meters long. Both sections have an internal cross section of 0.1016 x 0.381 meters. The test section contains two 0.14 meter circular windows for optical investigation of the test section's flow field. Mounted inside the test section, overlapping the circular windows, a 50 mm thick aluminum block forms the rear wall upon which the incident shock reflects.

The test section and the buffer section are mounted on rollers and are connected to the expansion section by means of hydraulic cylinders and connecting rods.

B. Pressure Transducer System

Previous detonation studies conducted with the Aeronautical and Astronautical Engineering Department's rectangular shock tube [5-7] have used a combination optical interferometer and light field schlieren system to measure the incident shock velocity, the reflected shock velocity, the density ratios across the shocks, and the ignition delay time. In this study

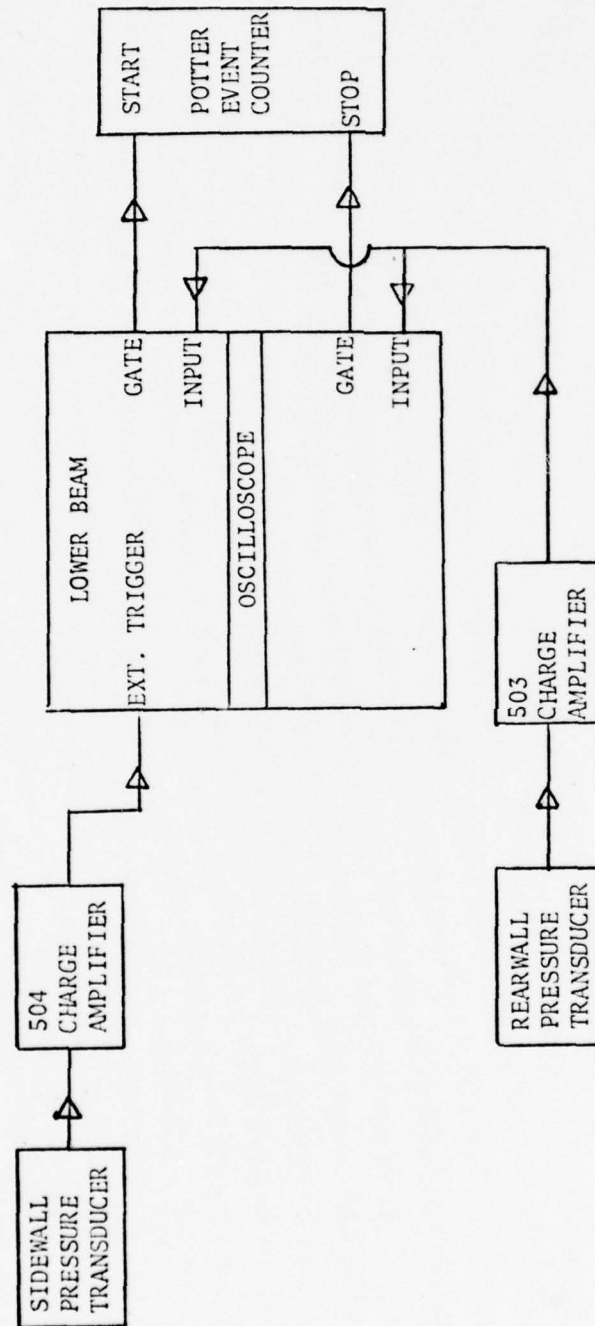
and its immediate predecessor [8], the incident shock velocity and the ignition delay time were measured using a pressure transducer system composed of two Kistler 103A piezoelectric transducers, a Kistler 503 charge amplifier, a Kistler 504 dual mode amplifier, a Tektronix 555 dual beam oscilloscope and camera, and a Potter 1.6 megacycle counter chronograph. A block diagram of the system is shown in Fig. 1.

One transducer is mounted in the shock tube's side wall (side wall transducer) 0.624 meters upstream of the aluminum block. As the incident shock passes the side wall transducer, the transducer produces a signal which triggers the oscilloscope's lower beam and starts the event counter. The second transducer is mounted in the center of the aluminum block (rear wall transducer); the signals produced from this transducer are recorded on the oscilloscope's lower and upper beams. When the incident shock strikes the aluminum block, the rear wall transducer produces a signal which triggers the oscilloscope's upper beam and stops the event counter. The oscilloscope's traces are recorded on 3000 ASA Polaroid film.

Example pictures are shown in Figs. 2 and 3. The oscilloscope's upper beam traces were set at sweep speeds varying from 10 $\mu\text{sec}/\text{cm}$ to 200 $\mu\text{sec}/\text{cm}$; this allowed reducible pressure-time histories of the ignition processes to be recorded. The oscilloscope's lower beam traces were set at a sweep speed of 200 $\mu\text{sec}/\text{cm}$; this allowed pressure-time histories from the incident shocks passing the side wall transducer through the detonation to be recorded.

C. Mixture Gases and Gauges

The propylene oxide used in this investigation was produced by Eastman, Rochester, NY. The gases used were high purity helium, extra dry oxygen



TRANSDUCER SYSTEM

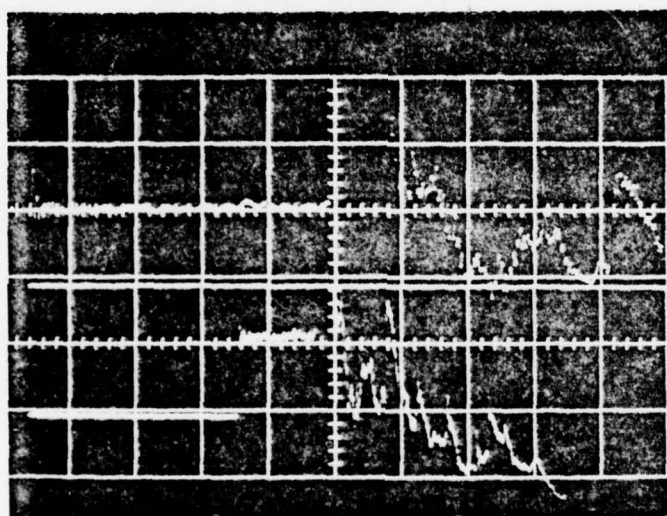
FIGURE I

OSCILLOSCOPE TRACT

$$\phi = 1.0$$

$$\% \text{C}_3\text{H}_6\text{O} = 18$$

(Strong Ignition)



UPPER BEAM:

VERT. DEFL. 1V/CM

SWEEP 50×10^{-6} SEC/CM

LOWER BEAM:

VERT. DEFL. 1V/CM

SWEEP 0.2×10^{-3} SEC/CM

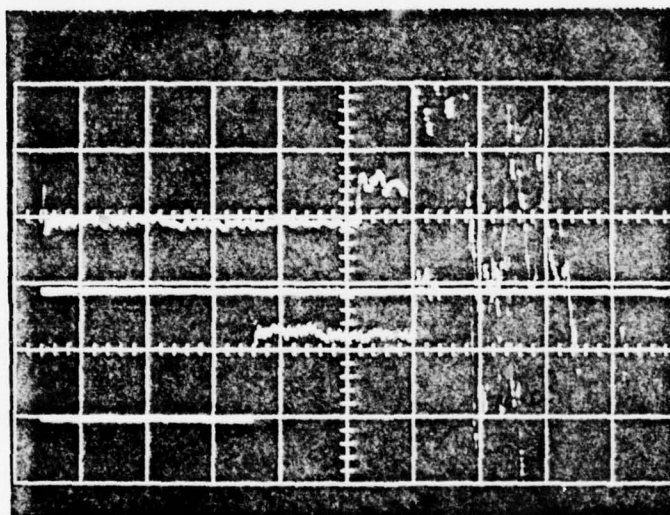
FIGURE II

OSCILLOSCOPE TRACE

$$\phi = 1.0$$

$$\% \text{C}_3\text{H}_6\text{O} = 18$$

(Mild Ignition)



UPPER BEAM:

VERT. DEFL. 1C/CM

SWEEP 100×10^{-6} SEC/CM

LOWER BEAM:

VERT. DEFL. 1V/CM

SWEEP 0.2×10^{-3} SEC/CM

FIGURE III

and prepurified nitrogen bottled by Linde. Two Wallace and Tiernan (800 and 1600 Torr) precision dial manometers were used to measure the pressures used in mixing, and to measure the pressures of the low pressure chamber and the high pressure chamber during an experiment.

III. PROCEDURE

A. Mixing

Six hours preceding a sequence of tests, the mixing chamber and the bleedoff chamber were evacuated below a pressure of 1.33 pascals and isolated. Using a syringe, liquid propylene oxide was injected into the evacuated mixing chamber through a compressed neoprene diaphragm. Using partial pressures, the excess propylene oxide was bled off; the appropriate amounts of nitrogen and oxygen were then added to obtain the desired mixtures listed in Table 1. For safety purposes, the total pressure of the test mixture in the mixing chamber was maintained below 5.45×10^4 pascals (410 Torr).

B. Test Run

Preparation for a test run began with the insertion of a diaphragm between the high pressure (buffer) chamber and the low pressure chamber of the shock tube; 76.2 μm acetate diaphragms were used for driving pressures under 1.15×10^5 pascals while 127 μm acetate diaphragms were used for driving pressures over 1.15×10^5 pascals. The shock tube was then evacuated; during this time the electronics were switched on and allowed to warm up. When the shock tube pressure, measured by an Alphatron Gauge, reached a pressure lower than 10 pascals, the high pressure chamber was isolated and filled with helium. As the high pressure chamber's pressure neared three quarters the driving pressure, the low pressure chamber was isolated from the vacuum pump and filled with the test mixture to a pressure of 1.33×10^3 pascals (10 Torr). After allowing enough time for the test mixture to attain equilibrium, the temperature of the test mixture was recorded using a thermometer placed in the top of the shock tube near the test section. Just before rupturing the diaphragm,

TABLE 1
 PROPYLENE OXIDE-OXYGEN-NITROGEN
 TEST MIXTURES

MIXTURE NUMBER	FUEL EQUIVALENCE RATIO	PERCENTAGE			PERCENTAGE			GAUGE PARTIAL PRESSURES (torr)		
		C_3H_6O	O_2	N_2	C_3H_6O	O_2	N_2	C_3H_6O	O_2	N_2
1	1.0	18	72	10	72	288	40	72	288	40
2	1.25	21.429	68.571	10	75	240	35	75	240	35
3	0.8	15	75	10	60	300	40	60	300	40
4	1.0	16	64	20	64	256	80	64	256	80

all equipment was rechecked and set; the oscilloscope's camera shutter was then opened.

After the shot was taken the oscilloscope's camera shutter was closed, the camera film developed, the Potter event counter time was recorded and the shock tube was cleaned and prepared for another experiment.

C. Data Reduction

The Potter event counter time and the test mixture's initial temperature, pressure and composition were used as input for the computer program SH3.F4. The program initially calculates the incident shock velocity by dividing the distance between the side wall and the rear wall transducers by the time measured on the Potter counter. Using the incident shock velocity and the other inputted data, the program then proceeds to calculate and output the temperature and the concentrations of propylene oxide, oxygen and nitrogen behind the reflected shock. A description of the program is given in Appendix A.

There were two modes of ignition observed in this investigation, an occurrence which has been studied in H_2-O_2 detonation by Meyer and Oppenheim [9]. Figure 2 represents a strong ignition; on the upper beam trace the instantaneous appearance of the strong pressure spike is associated with a one-dimensional detonation initiation. Figure 3 represents a mild ignition; on the upper beam trace the appearance of the mild pressure spike is associated with the formation of distinct flame kernels, the appearance of a relatively constant pressure following the mild pressure spike is associated with the growth of the flame kernels, and the appearance of the second pressure spike is associated with the formation of a detonation wave. The ignition

delay time was calculated from the distance between the triggering and the first pressure spike recorded on the upper beam trace, the first pressure spike representing the beginning of ignition in both strong and mild ignitions.

Presented in Tables 2-5 are the reflected shock properties calculated from SH3.F4 and the ignition delay times measured from the oscilloscope's upper beam traces.

Plots of the ignition delay times versus the reciprocal of the reflected shock temperatures for each mixture are presented in Figs. 4-7.

TABLE 2
KINETIC DATA FOR SHOCK TUBE RUNS

Fuel Equivalence Ratio = 1.0
C₃H₆O Percentage = 18%

10 ³ /T	(C ₃ H ₆ O)	(O ₂)	(N ₂)	Initiation Delay Time
°K ⁻¹	10 ⁻² K-mol/m ³	10 ⁻² K-mol/m ³	10 ⁻² K-mol/m ³	10 ⁻⁶ sec
0.955	0.23881	0.95523	0.13267	230.0
0.874	0.26965	1.07860	0.14981	44.0
0.858	0.27613	1.10450	0.15340	26.5
0.928	0.24852	0.99408	0.13807	110.0
1.035	0.21102	0.84406	0.11723	1180.0
0.888	0.27237	1.08950	0.15132	65.0
0.943	0.25127	1.00510	0.13959	152.5
0.968	0.24210	0.96841	0.1345	460.0
0.982	0.23651	0.94604	0.13139	520.0
0.980	0.23964	0.95856	0.13313	435.0
0.993	0.23283	0.93130	0.12935	675.0
0.867	0.27617	1.10470	0.15343	48.0
0.885	0.26663	1.06650	0.14813	58.0
1.035	0.21612	0.86450	0.12007	1140.0
1.024	0.2230	0.88921	0.12350	1060.0
0.966	0.23862	0.95447	0.13256	205.0
0.920	0.25316	1.01260	0.14064	88.0
0.902	0.25981	1.03920	0.14434	64.0
0.932	0.24729	0.98914	0.13738	110.0
0.973	0.23204	0.92814	0.12891	227.5
0.996	0.23665	0.94659	0.13147	350.0
0.965	0.23596	0.94384	0.13109	192.5
0.922	0.25697	1.02790	0.14276	162.5
0.970	0.23329	0.93314	0.12960	255.0
0.920	0.24937	0.99750	0.13854	98.0
1.037	0.20784	0.83139	0.11547	1050.0
1.026	0.21003	0.84014	0.11669	800.0
0.969	0.22543	0.90174	0.12524	250.0
0.904	0.24712	0.98850	0.13729	77.0
0.992	0.22553	0.90133	0.12518	420.0*
0.995	0.22901	0.91605	0.12723	435.0*
0.975	0.23797	0.94988	0.13193	300.0*
1.022	0.20940	0.83758	0.11633	490.0*

* Mild ignitions.

TABLE 3
KINETIC DATA FOR SHOCK TUBE RUNS

Fuel Equivalence Ratio = 1.25
C₃H₅O Percentage = 21.429%

$10^3/T$	(C ₃ H ₅ O)	(O ₂)	(N ₂)	Initiation Delay Time
$^{\circ}\text{K}^{-1}$	10^{-2} K-mol/m ³	10^{-2} K-mol/m ³	10^{-2} K-mol/m ³	10^{-6} sec
1.035	0.28392	0.90854	0.13250	880.0
0.966	0.31635	1.01230	0.14763	195.0
0.936	0.33678	1.07770	0.15717	116.0
0.985	0.31091	0.99493	0.14509	235.0
1.008	0.29778	0.95289	0.13896	355.0
1.064	0.27134	0.86828	0.12662	1070.0
0.923	0.34419	1.10140	0.16062	72.0
0.955	0.32720	1.04700	0.15269	148.0
1.061	0.27730	0.88737	0.12941	1000.0
0.993	0.30550	0.97760	0.14257	280.0*
1.065	0.28915	0.92528	0.13494	1040.0
1.013	0.31027	0.99288	0.14479	310.0
0.954	0.33586	1.07480	0.15674	134.0
1.019	0.29709	0.95068	0.13864	360.0
1.027	0.29146	0.93266	0.13601	555.0
0.984	0.31600	1.01120	0.14747	245.0
0.955	0.32086	1.02670	0.14973	160.0
1.023	0.28470	0.90934	0.13261	590.0
1.033	0.28817	0.92214	0.13448	875.0
0.964	0.30695	0.98224	0.14324	195.0
1.041	0.27162	0.86919	0.12676	960.0
1.014	0.29147	0.93269	0.13602	340.0
0.983	0.30566	0.97810	0.14264	240.0
0.933	0.32891	1.05250	0.15349	117.0
1.038	0.27724	0.88716	0.12938	970.0
1.018	0.30183	0.97584	0.14085	350.0
0.894	0.35912	1.14920	0.16759	93.0
0.900	0.24234	1.09550	0.15976	99.0
0.895	0.35469	1.13500	0.16552	94.0

* Mild ignitions

TABLE 4

KINETIC DATA FOR SHOCK TUBE RUNS

Fuel Equivalence Ratio = .8

 C_3H_6O Percentage = 15%

$10^3/T$	(C_3H_6O)	(O_2)	(N_2)	Initiation Delay Time
$^{\circ}K^{-1}$	$10^{-2} \text{ K-mol/m}^3$	$10^{-2} \text{ K-mol/m}^3$	$10^{-2} \text{ K-mol/m}^3$	10^{-2} sec^3
1.040	0.15971	0.79854	0.10647	1210.0
0.885	0.19915	0.99576	0.13277	62.0
0.918	0.18882	0.94410	0.12588	114.0
1.013	0.16334	0.81669	0.10889	635.0
0.985	0.16536	0.82678	0.11024	355.0
0.976	0.19431	0.97153	0.12954	48.0
0.935	0.17727	0.88637	0.11818	155.0
1.011	0.15711	0.78555	0.10474	810.0
0.892	0.18983	0.94814	0.12655	59.0
1.030	0.15410	0.77049	0.10273	1080.0
0.890	0.18836	0.94182	0.12558	61.0
0.950	0.17265	0.86317	0.11509	190.0
0.906	0.18753	0.93766	0.12502	75.0
0.922	0.18243	0.91215	0.12162	125.0
0.962	0.17077	0.85386	0.11385	240.0
0.884	0.19545	0.97727	0.13030	44.0
0.929	0.18727	0.93636	0.12485	136.0
0.932	0.18968	0.94842	0.12646	104.0
0.954	0.18248	0.91239	0.12165	195.0
0.968	0.17722	0.88610	0.11815	260.0
0.991	0.17171	0.85856	0.11447	435.0*
0.999	0.16085	0.80474	0.10730	480.0*
1.006	0.15936	0.79681	0.10624	490.0*
1.020	0.15573	0.77863	0.10382	690.0*

* Mild ignitions

TABLE 5
KINETIC DATA FOR SHOCK TUBE RUNS

Fuel Equivalence Ratio = 1.0
C₃H₆O Percentage = 16%

10 ³ /T	(C ₃ H ₆ O)	(O ₂)	(N ₂)	Initiation Delay Time
°K ⁻¹	10 ⁻² K-mol/m ³	10 ⁻² K-mol/m ³	10 ⁻² K-mol/m ³	10 ⁻⁶ sec
0.903	0.21249	0.84997	0.26562	66.0
0.902	0.21322	0.85288	0.26653	62.0
0.943	0.19970	0.79879	0.24962	175.0
0.915	0.21342	0.85366	0.26679	83.0
0.951	0.20127	0.80507	0.25159	172.5
0.974	0.19288	0.77153	0.24110	250.0
1.032	0.17558	0.70234	0.21948	1020.0
0.991	0.18798	0.75191	0.23497	332.5
0.926	0.20448	0.81792	0.25560	122.0
0.901	0.21111	0.84445	0.26389	75.0
0.982	0.18731	0.74922	0.23413	277.5
0.953	0.19262	0.77048	0.24077	150.0
0.898	0.21266	0.85063	0.26582	72.0
0.925	0.20338	0.81350	0.25422	132.0
0.978	0.18711	0.74845	0.23389	230.0
1.014	0.17787	0.71149	0.22234	425.0*
1.001	0.18421	0.73683	0.23026	320.0*
1.023	0.17825	0.71300	0.22281	500.0*
1.017	0.17654	0.70617	0.22068	680.0*
1.029	0.17115	0.68462	0.21394	730.0*
0.987	0.18604	0.74416	0.23255	300.0*
1.024	0.17150	0.68599	0.21437	595.0
1.029	0.16981	0.67924	0.21226	885.0
0.946	0.19088	0.76352	0.19088	125.0
0.949	0.18787	0.75149	0.23484	142.5

* Mild ignition

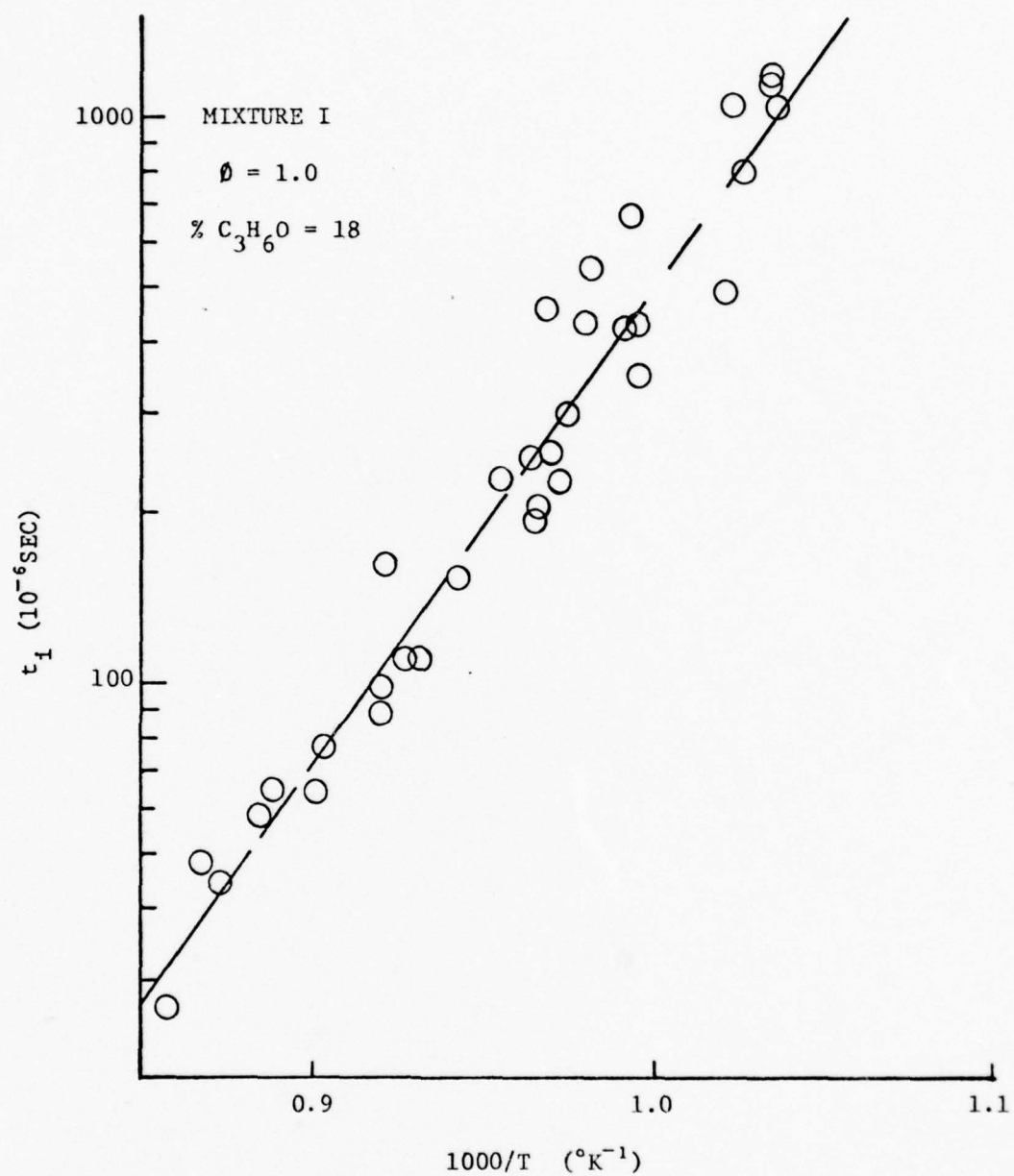
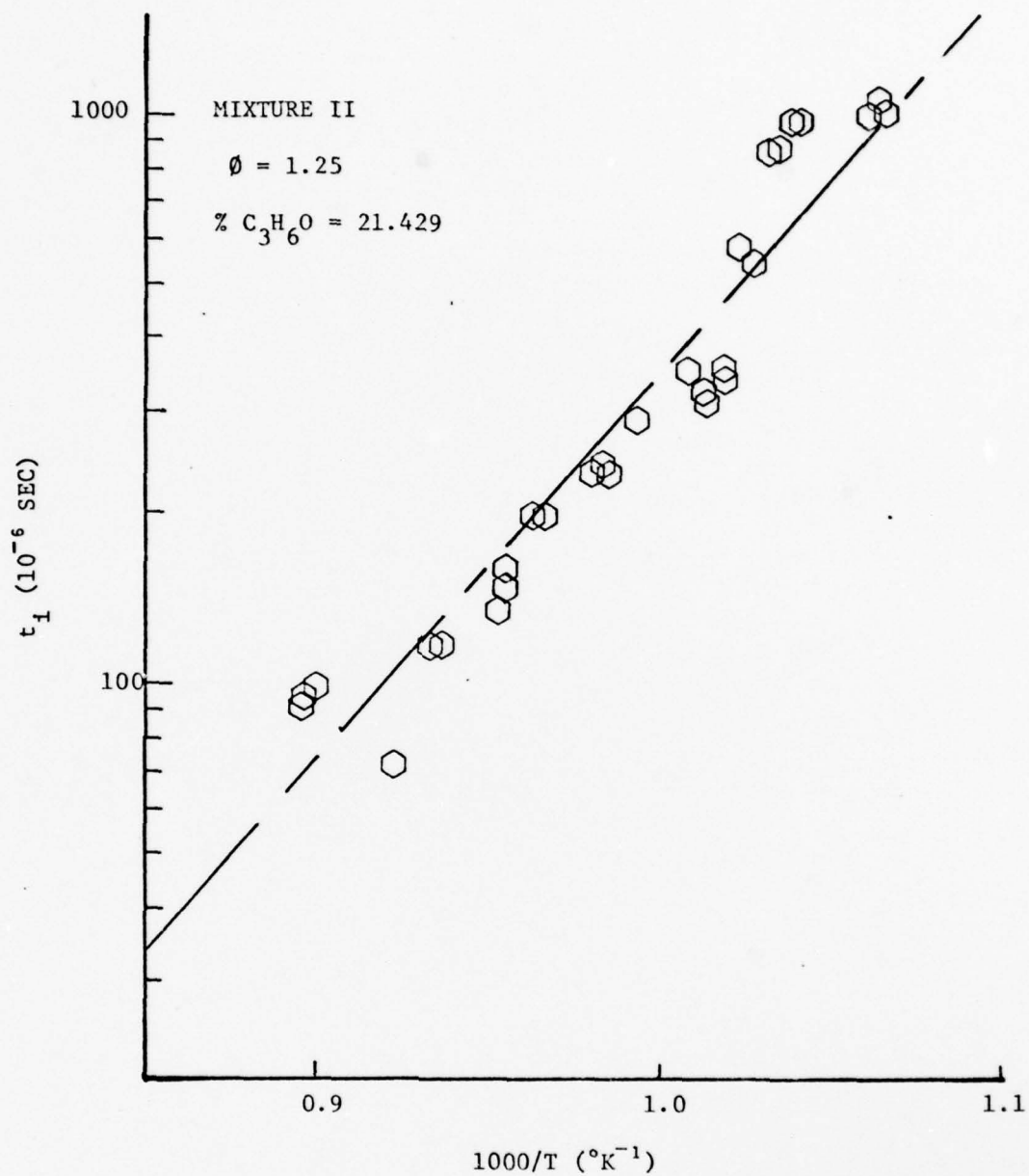
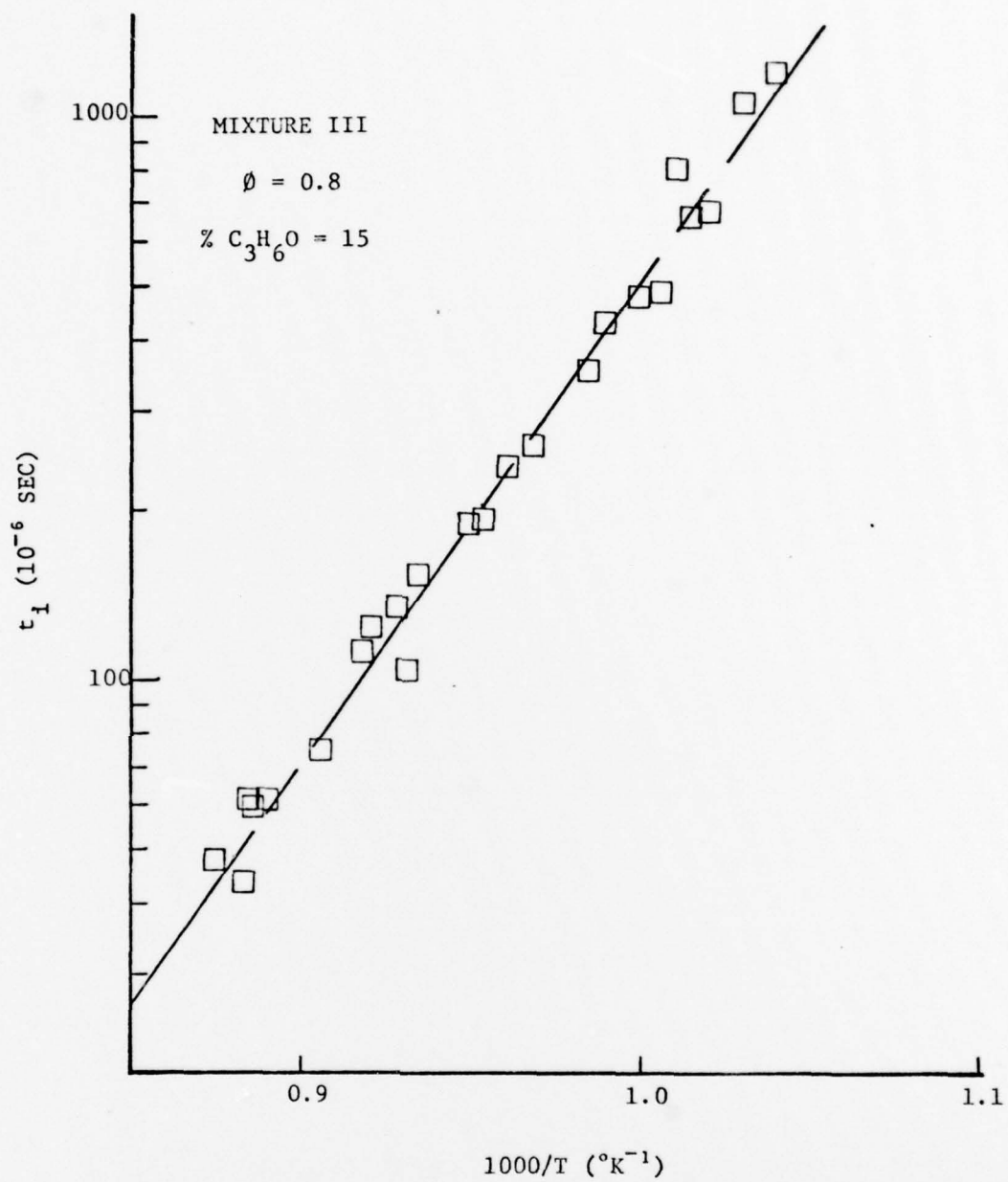
IGNITION DELAY TIME VS. 10^3 /REFLECTED SHOCK TEMPERATURE

FIGURE IV



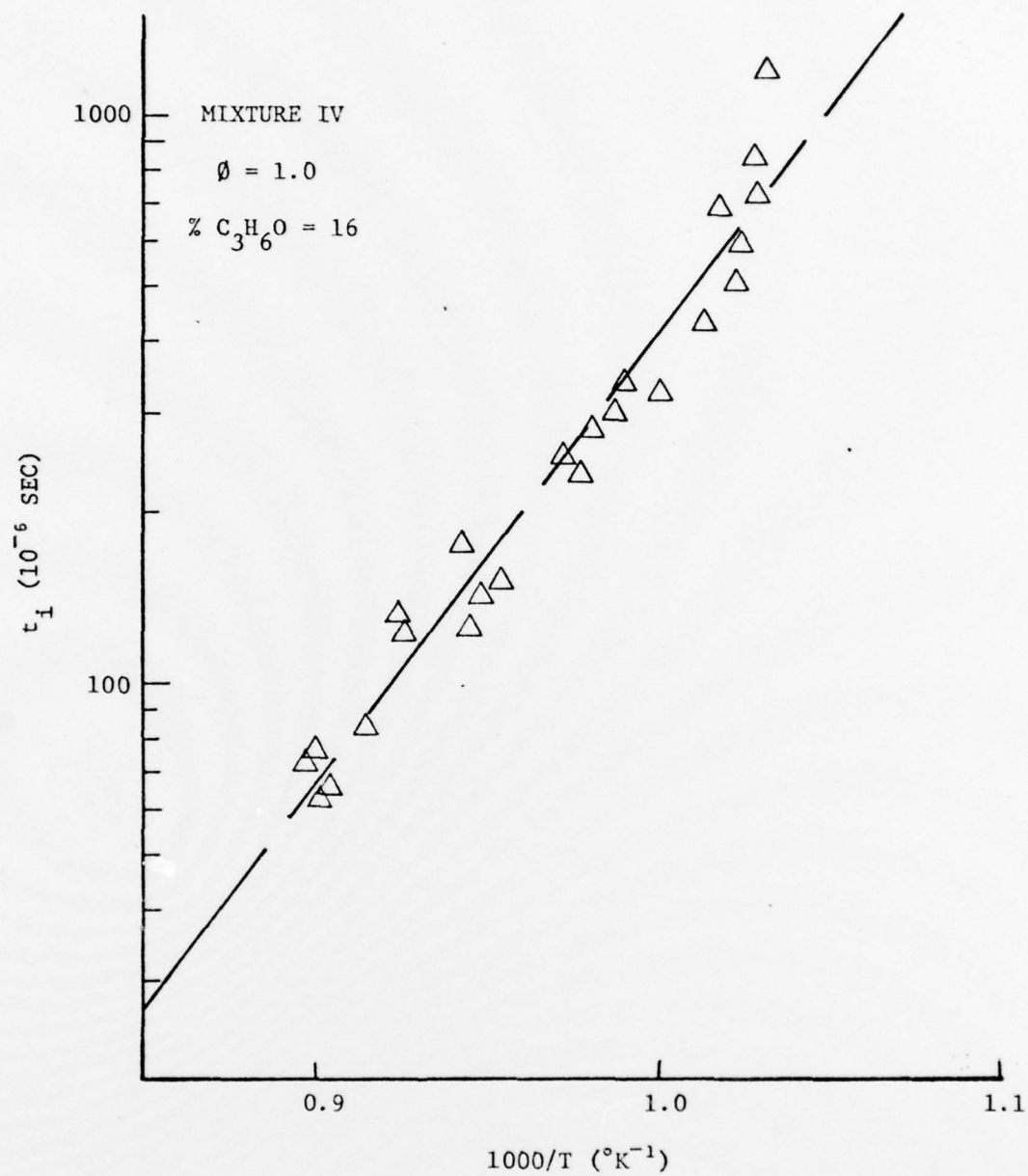
IGNITION DELAY TIME VS. $10^3/\text{REFLECTED SHOCK TEMPERATURE}$

FIGURE V



IGNITION DELAY TIME VS. 10^3 /REFLECTED SHOCK TEMPERATURE

FIGURE VI



IGNITION DELAY TIME VS. $10^3/\text{REFLECTED SHOCK TEMPERATURE}$

FIGURE VII

IV. RESULTS AND DISCUSSION

The goal of this investigation was to develop a model relating the ignition delay time to the temperature and the gas concentrations in propylene oxide-oxygen-nitrogen detonations. Using the multiple regression routine in Appendix B, the Arrhenius rate relation for calculating the ignition delay time in seconds was found to be:

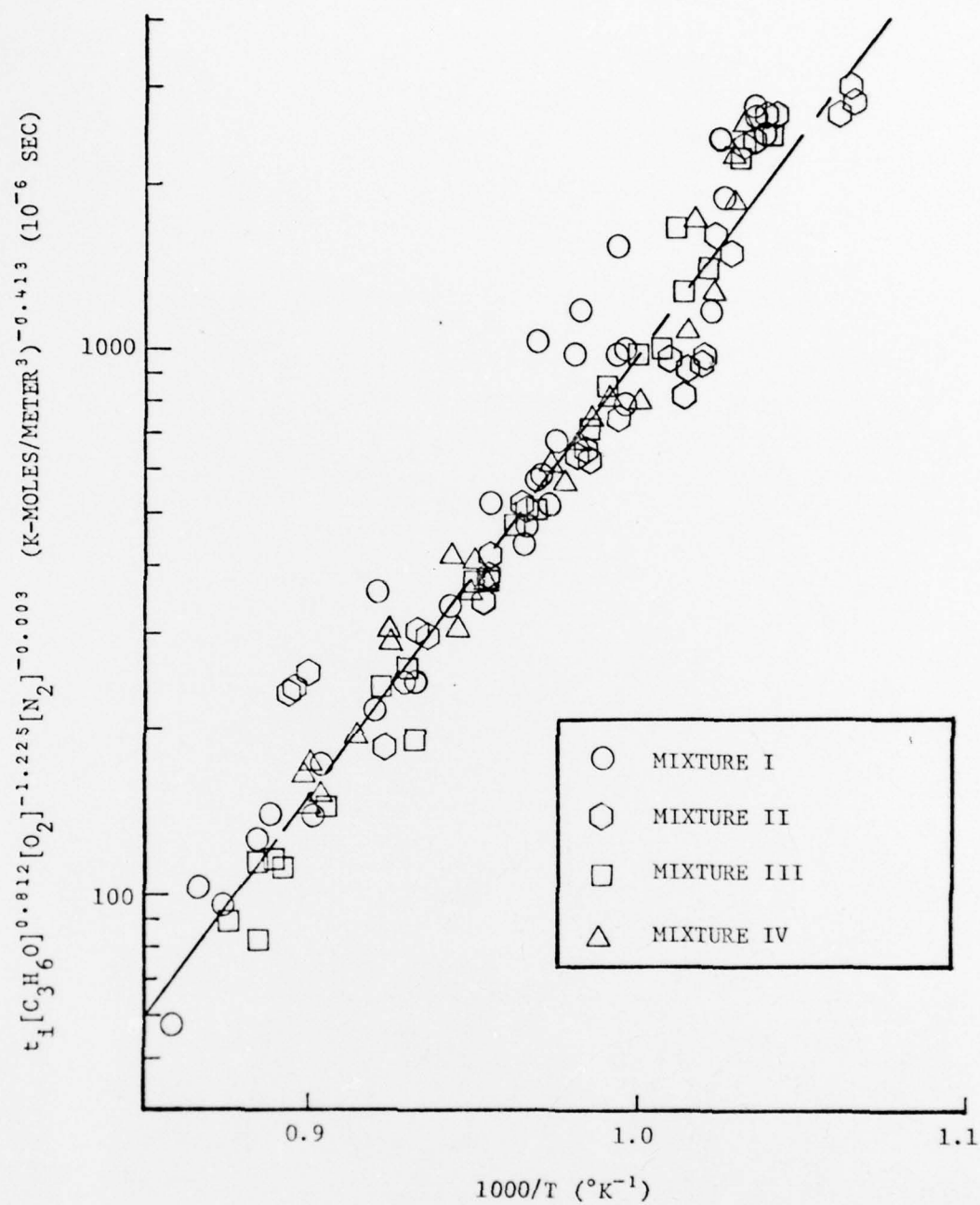
$$t_i = 6.203 \times 10^{-12} \exp\left\{\frac{18.924 \times 10^3}{T}\right\} [C_3H_6O]^{-0.812} [O_2]^{1.225} [N_2]^{0.003}$$

The activation energy, using a 90% confidence interval, was found to be $(1.573 \pm 0.209) \times 10^5$ Joules/mole.

Two checks were made to determine the reliability of these results. First, theory indicates that nitrogen, because of its high dissociation energy, should act as an inert in the temperature ranges of this detonation study. As an inert, nitrogen should have a concentration dependency exponent near zero; the experimental concentration dependency exponent 0.003 is very satisfactory. Second, the four mixtures' kinetic data were reduced to a single line by plotting $t_i [C_3H_6O]^{0.812} [O_2]^{-1.225} [N_2]^{-0.003}$ versus $10^3/T$ in Fig. 8. The fit along the least squares was satisfactory.

The experimental Arrhenius rate relation indicates that propylene oxide concentration increases promote detonation while oxygen concentration increases inhibit detonation. In direct contrast C_1 - C_5 alkane research conducted by Burcat, Scheller, and Lifshitz [10] indicates that alkane concentration increases inhibit detonations.

Approximately 40% of the ignition within the temperature range 970 - 1025°K were mild ignitions. In an attempt to explain the differences



$$t_i [C_3H_6O]^{0.812} [O_2]^{-1.225} [N_2]^{-0.003} \text{ vs. } 1/T$$

ALONG THE LEAST SQUARES LINE

FIGURE VIII

between the mild ignitions and the strong ignitions, reference is made to the H_2-O_2 ignition studies by Meyer and Oppenheim [9], Voevodsky and Solouklyn [11], and Cohen and Larsen [12]. In these studies mild ignitions were characterized by the appearance of distinct flame kernels during the initial stages of ignition. The mild ignitions also occurred near the second explosion limit, where chain reaction sensitivity to gas-phase recombinations increases. In this investigation mild ignitions are assumed to occur near the second explosion limit. Because of the chain reactions sensitivity to gas-phase recombination, distinct flame kernels appear instead of a strong ignition. The rate of heat released from these flame kernels are too small to generate a strong pressure pulse, thus the weak pressure pulse found on the upper beam trace in Fig. 3.

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APPENDIX A

The program SH3.F4 is a revised version of the Fortran Program SH2.F4 [8], modified to handle propylene oxide-oxygen-nitrogen mixtures. The program inputs are: the test mixture-test run number, the test mixture's partial pressures, the shock tube mixture's initial temperature and initial pressure, and the Potter counter time measurements. The SH3.F4 program outputs are: the fuel equivalence ratio, the fuel percentage, the average molecular weight, the specific heat ratio, the incident Mach number and shock conditions, and the kinetic parameters.

The equations used in solving the incident and reflected shock condition assume a one-dimensional, inviscid, steady state, non-reactive, ideal gas flow system. The shock equations used in SH2.F4 and SH3.F4 programs are derived in Reference 8. Essentially the program is an iteration scheme which assumes a temperature behind a shock wave, calculates a shock velocity, and compares this value with known conditions. For convergence the calculated square of the incident shock velocity must equal the square of the measured incident shock velocity within one part in 10^4 , and the calculated velocity at the back wall must be less than one part in 10^4 of the incident flow velocity.

FORTRAN PROGRAM SH3.F4

```

      IMPLICIT REAL*8 (A-H,P-Z)
      REAL*8 LAMDA,MACH
      COMMON A, AK, AKP( 10 ), AMMW, AMU, AMW( 30 ),
      *      CP, CPDT( 30 ), CPN, CPP( 30 ), D,
      *      EPSK( 30 ), FREE( 30 ), GAMMA, H, HM,
      *      HO( 30 ), HCO( 30 ), HT, PP,
      *      S, SIGMA( 30 ), SM, SO( 30 ), SPECIE( 30 ),
      *      ST( 30 ), STICH( 10,30 ), X( 30 )

      LIN=0.0
      SPECIE(1)='N2'
      SPECIE(2)='O2'
      SPECIE(3)='CO2H6O'
      CALL LOADCO(3,IER1)
      IF (IER1.NE.0) TYPE 140
65  CONTINUE
      TYPE 100
      ACCEPT 200,RUN
      IF (RUN.LT.0.0) STOP
      TYPE 110,RUN
      LUN=RUN
      IF (LIN.EQ.LUN) GOTO 60
      LIN=LUN
      TYPE 120
      ACCEPT 220, PO, PN2, PO2
      X(1)=PN2
      X(2)=PO2
      X(3)=PO
      XT=X(1)+X(2)+X(3)
      DO 30 I=1,3
30  X(I)=X(I)/XT
      EOR=4.*X(3)/X(2)
      PC3=X(3)*100.
60  CONTINUE
      TYPE 130, EOR, PC3
      ACCEPT 210, TI, PI
      T=(TI+450.57)*5./2.
      P=PI/760.
      CALL THERMO(T,P,IER2,IER3)
      IF (IER2.NE.0) TYPE 300
      IF (IER3.NE.0) TYPE 600
      TYPE 150, PI, TI, AMMW, GAMMA
      CON=4.186D7
      H1=HM*CON
      R=1.986*CON/AMMW
      P1=P
      T1=T
      WRITE(5,6)
      READ(5,7) TIME
      TIME=TIME*1.0D-3
      U1=62.389/TIME
      MACH=U1/A
      WRITE(5,15) MACH
      U1SQ=U1*U1

      CALCULATE TEMP BEHIND INCIDENT SHOCK
      T33=400.
      T31=1000.
      DO 22 I=1,25
      T21=T20
      T20=T33

```

```

T33=T31
U11SQ=U10SQ
CALL THERMO (T20,P,IER2,IER3)
IF (IER3.NE.0) WRITE(5,600)
HM=HM*CON
LAMDA=((2*(HM-H1)-R*(T20-T1))/(R*T20)+
*DSQRT(((2*(HM-H1)-R*(T20-T1))/(R*T20))**2+4*T1/T20))/2
U20SQ=2*(HM-H1)/(LAMDA**2-1)
U10SQ=(LAMDA**2)*U20SQ
IF (J.EQ.1) GOTO 22
IF (DABS((U11SQ-U10SQ)/U10SQ).LT.0.0001) GO TO 20
T33=T20-(T21-T20)*(U10SQ-U1SQ)/(U11SQ-U10SQ)
22 CONTINUE
WRITE(5,50)
50 FORMAT('TEMP DID NOT CONVEGRE')
STOP
20 CONTINUE
PR=PI*LAMDA*T20/T1
TYPE 170,T20,PR
170 FORMAT(2X,'INCIDENT SHOCK CONDITIONS ARE',/5X,'TEMPERAT
*URE= 'F9.2,' DEGREES K: PRESSURE= 'F8.2,' TORR'/)

CALCULATE TEMP BEHIND REFLECTED SHOCK
UPR=DSQRT(U10SQ)-DSQRT(U20SQ)
T1=T20
T22=T20
H1=HM
T33=T20+100.
T31=1500.
DO 33 J=1,25
T21=T20
T20=T33
T33=T31
UP1=UP0
CALL THERMO (T20,P,IER2,IER3)
IF (IER3.NE.0) WRITE(5,600)
HM=HM*CON
LAMDA=((2*(HM-H1)-R*(T20-T1))/(R*T20)+
*DSQRT(((2*(HM-H1)-R*(T20-T1))/(R*T20))**2+4*T1/T20))/2
U20SQ=2*(HM-H1)/(LAMDA**2-1)
U10SQ=(LAMDA**2)*U20SQ
UP0=DSQRT(U10SQ)-DSQRT(U20SQ)
IF (J.EQ.1) GOTO 33
IF (DABS((UP0-UPR)/UPR).LT.0.0001) GO TO 70
T33=T20-(T21-T20)*(UP0-UPR)/(UP1-UP0)
33 CONTINUE
WRITE(5,55)
55 FORMAT('TEMP DID NOT CONVERGE, REFLECTED SHOCK')
STOP
70 CONTINUE
PRR=PR*LAMDA*T20/T22
PT=1000./T20
CI=PR*1.603D-5/T20
CX2=CI*X(2)
CX3=CI*X(3)
CX1=CI*X(1)
TYPE 180,T20,PRR,PT,CX2,CX3,CX1
GO TO 65
1 FORMAT('LIST SPECIES AND MOLE FRACTIONS')
2 FORMAT('/MOLE FRACTIONS DO NOT ADD UP TO 1.0')

```

```

3  FORMAT(2F5.1)
4  FORMAT(// 'NUMBER OF SPECIES =',I3)
5  FORMAT(// 'TEMPERATURE IS OUTSIDE RANGE OF THERMO')
6  FORMAT(// 'HEAD TIME MEASUREMENT IN MILLISECONDS')
7  FORMAT(2F7.4)
8  FORMAT(' PICK INITIAL GUESS OF TEMP BEHIND SHOCK IN DEGREE KELVIN
1  ')
9  FORMAT(' READ INITIAL TEMPERATURE AND PRESSURE (2F5.1)')
10 FORMAT(' TEMP BEHIND INCIDENT SHOCK',F8.2,' DEGREE KELVIN')
11 FORMAT(' TEMP BEHIND REFLECTED SHOCK',F8.2,' DEGREE KELVIN')
12 FORMAT(' 12X, INCIDENT MACH NUMBER',F5.2)
13  FORMAT(' INCIDENT SHOCK VELOCITY',F10.3,'CM/SEC')
100 FORMAT(// 'SHOCK TUBE RUN NO?',F7.2)
110 FORMAT(// 'SHOCK TUBE RUN NUMBER IS',F7.2)
120 FORMAT(// 'ENTER PARTIAL PRESSURE OF PROPYLENE
* OXIDE, NITROGEN, AND OXYGEN, 3F5.1//')
210 FORMAT(2F5.1)
220 FORMAT(3F5.1)
130 FORMAT(' FUEL EQUIVALENC RATIO IS',F6.3
* // 'PERCENT PROPYLENE OXIDE IS',F7.3// 'ENTER INITIAL
* TEMPERATURE, DEGREES F.// ' AND INITIAL PRESSURE,
* TORR: 2F5.1//')
140 FORMAT(' SPECIES NOT LOADED CORRECTLY')
150 FORMAT(' INITIAL CONDITIONS: PRESSURE= ',F6.2,' TORR;
* TEMP= ',F6.2,' DEGREES F.// 12X ' AVE MOL WT= ',F6.3,
* ' G/MOLE',5X,' GAMMA= ',F6.3//)
160 FORMAT(3F16.6)
180 FORMAT(1X ' REFLECTED SHOCK CONDITIONS ARE'//
* 12X ' TEMPERATURE= ',F8.2,' DEGREES K: PRESSURE= '
* 12X ' TORR'// 10X ' KINETIC PARAMETERS ARE'//
* 12X ' 1000./7 = ',F6.3,
* 12X ' (O2) = ',D15.5,' MOLES/CC//
* 12X ' (C3H6O) = ',D15.5,' MOLES/CC//
* 12X ' (H2) = ',D15.5,' MOLES/CC'///)
200 FORMAT(F7.2)
300 FORMAT(// 'SUM OF MOLE FRACTIONS NOT UNITY')
500 FORMAT(2X,10A6)
600 FORMAT(// 'TEMPERATURE OUTSIDE RANGE')
END

```

INPUT - OUTPUT

FORTRAN PROGRAM SH3.F4

```

SHOCK TUBE RUN NO 7, F7.2
1606.03

SHOCK TUBE RUN NUMBER IS 1606.03
FUEL EQUIVALENCE RATIO IS 1.000
PERCENT PROPYLENE OXIDE IS 16.000

ENTER INITIAL TEMPERATURE, DEGREES F.
AND INITIAL PRESSURE, TORR: 2F5.1

86.2 10.0
INITIAL CONDITIONS: PRESSURE= 10.00 TORR TEMP= 86.20 DEGREES F
AVE MOL WT= 35.375 G/MOLE GAMMA= 1.298

READ TIME MEASUREMENT IN MILLISECONDS
.624375
INCIDENT MACH NUMBER 3.29
INCIDENT SHOCK CONDITIONS ARE
TEMPERATURE= 696.33 DEGREES K: PRESSURE= 124.19 TORR

REFLECTED SHOCK CONDITIONS ARE
TEMPERATURE= 1056.65 DEGREES K: PRESSURE= 786.39 TORR

KINETIC PARAMETERS ARE
1000./t = 0.946
(O2) = 0.763520-05 MOLES/CC
(C3H6O)= 0.190880-05 MOLES/CC
(N2) = 0.238600-05 MOLES/CC

```


APPENDIX B

The multiple regression routine in a Soupac Program run on the University of Illinois 360 computer system. The program is based on the matrixed linear regression model presented in Neter and Wasserman [13].

A general linear regression model can be expressed as:

$$y_i = a_0 + a_1 x_{i,1} + a_2 x_{i,2} \cdots a_{p-1} x_{i,p-1} + e_i$$

e_i is the random error term. Rewritten in matrix form, the model becomes:

$$\begin{matrix} Y & = & X & A & + & E \\ nx1 & & nxp & px1 & & nx1 \end{matrix} \quad (1)$$

The least squares estimators of A are:

$$\hat{A} = (X'X)^{-1}X'Y \quad (2)$$

The sample variance is equal to:

$$S^2 = (Y'Y - \hat{A}X'Y)/n-p \quad (3)$$

In this ignition delay time study, the multiple regression model chosen was the Arrhenius rate relation:

$$t_{ij} = A \exp[E_o/RT_j] [C_3H_6O]_j^a [O_2]_j^b [N_2]_j^c e_j \quad (4)$$

t_i = ignition delay time (sec)

A = pre-exponential constant

E_o = activation energy (Joules/mole)

T = reflected shock temperature ($^{\circ}$ K)

R = universal gas constant (8.314 Joules/mole- $^{\circ}$ K)

a,b,c = exponents

[] = concentrations (K-moles/meter³)

e = random error term

Linearization of the regression model yields:

$$\ln t_{ij} = \ln A + (E_o/R)(1000/T_j) + a \ln[C_3H_6O] + b \ln[O_2]_j + c \ln[N_2]_j \quad (5)$$

Essentially the Soupac Program solves the matrix equations 2 and 3 after equation 5 is put in the form of equation 1. The Soupac Program calculations for the least squares estimation of the parameters in equation 5 are:

$$\begin{array}{c|c|c} \ln \hat{A} & & -25.806 \\ \hat{E}_o/R & & 18.925 \\ \hat{a} & \equiv & -0.812 \\ \hat{b} & & 1.225 \\ \hat{c} & & 0.003 \end{array}$$

For $n = 111$ and $p = 5$, the sample variance (s^2) equaled 0.05.

A 90% confidence interval was calculated for \hat{E}_o/R using the F distribution table in Reference 13 and the confidence interval relation:

$$|\hat{E}_o/R - E_o/R| \leq (F_{.90, 1, 106})^{1/2} \hat{\sigma}_{\hat{\psi}}$$

$$(\hat{\sigma}_{\hat{\psi}})^2 = [0 \ 1 \ 0 \ 0 \ 0] (X'X)^{-1} \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} s^2$$

The confidence interval for \hat{E}_o/R is $18.925 \pm 2.52 \text{ } ^\circ K^{-1}$.

